

Novel Thioborates of Cesium: Cs_3BS_3 and Li_2CsBS_3

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Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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Thioborates, Boron, Crystal Structures

The new compounds Li_2CsBS_3 and Cs_3BS_3 were prepared from the metal sulfide(s), amorphous boron and sulfur in solid state reactions at high temperatures. The crystal structures were determined by single crystal X-ray diffraction experiments. The purity of the products was proved by powder diffraction. Li_2CsBS_3 crystallizes in the orthorhombic space group $Pnma$ (no. 62) with $a = 10.004(2)$, $b = 8.000(2)$, $c = 8.082(2)$ Å, and $Z = 4$, while Cs_3BS_3 is isotypic to Rb_3BS_3 in the monoclinic space group $P2_1/c$ (no. 14) with $a = 10.397(1)$, $b = 6.660(1)$, $c = 13.618(1)$ Å, $\beta = 101.31(1)^\circ$, and $Z = 4$. Both compounds contain isolated $[\text{BS}_3]^{3-}$ anions with boron in a trigonal-planar coordination.

Introduction

Numerous thio- and selenoborates have been synthesized and characterized in recent years due to improved preparation techniques [1, 2]. Binary boron sulfides and selenides [1, 3 - 5] as well as ternary and quaternary thio- and selenoborates contain boron in a trigonal-planar coordination. In the latter various novel types of chalcogenoborate anions are observed. Typical examples are the small, highly charged anion entities BS_3^{3-} [6 - 8], BSe_3^{3-} [9], $\text{B}_2\text{S}_4^{2-}$ [10], $\text{B}_2\text{S}_5^{2-}$ [11], and $\text{B}_3\text{S}_6^{3-}$ [8, 12 - 14] which are characteristic structural features in chalcogenoborates of alkali and alkaline earth metals. It is well known that in addition to large cations such as strontium and barium, smaller alkali ions, especially lithium, can be incorporated in thioborate structures [7, 8, 15]. This is of special importance for the physical properties of these compounds, e.g. for the ionic conductivity observed in some lithium thioborates [16, 17]. In this context, more detailed knowledge on the possible substitution of lithium by its heavier homologues in the aforementioned compounds as well as on the possible insertion of alkali metals in larger framework structures is necessary. Such networks are also found in several thioborate structures containing lithium, sodium or even silver cations [15, 18, 19]. As systematic studies are hitherto only available for

a few selected ternary and quaternary phases, further investigations are underway, *i. e.* several projects in our group are focussing on chalcogenoborates containing heavy alkali metals and their physical properties.

Although orthothioborates containing alkali metals are known with lithium, sodium, potassium and rubidium [6, 7] the corresponding cesium compound or even cesium containing orthothioborates could not be synthesized for years. Previous examinations on the quasi-binary cross sections $\text{Cs}_2\text{S}/\text{B}_2\text{S}_3$ were based on glassy or microcrystalline products [20, 21] but crystal structure determinations were unavailable. The systematic exchange of lithium vs. cesium in the synthesis of lithiumthioborates resulted in the new structure of composition Li_2CsBS_3 . Furthermore the synthesis of Cs_3BS_3 was successful due to improved preparation techniques for Cs_2S and refined temperature programs.

Experimental Section

Syntheses

The synthesis of well-defined and highly pure boron chalcogen compounds is rather difficult because of the high reactivity of boron chalcogenides formed *in situ* towards a variety of container materials at elevated temperatures. The fused silica tubes usually employed for solid state reactions

	Li ₂ CsBS ₃	Cs ₃ BS ₃
Formula weight [g·mol ⁻¹]	253.78	505.72
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	<i>Pnma</i> (no. 62)	<i>P2₁/c</i> (no. 14)
Unit cell dimensions	<i>a</i> = 10.004(2) Å <i>b</i> = 8.000(2) Å <i>c</i> = 8.082(2) Å	<i>a</i> = 10.397(1) Å <i>b</i> = 6.660(1) Å <i>c</i> = 13.618(1) Å <i>β</i> = 101.31(1)°
Volume [Å ³]	646.8(3)	924.7(2)
<i>Z</i>	4	4
Density (calculated) [g·cm ⁻³]	2.61	3.63
Absorption coefficient [mm ⁻¹]	6.55	12.34
<i>F</i> (000)	456	872
Crystal size [mm ³]	0.25 × 0.18 × 0.03	0.23 × 0.16 × 0.10
Crystal colour	colourless / prism	colourless / prism
Measurement device	SIEMENS P3	BRUKER AXS Apex
Absorption correction method	<i>ψ</i> -scans	SADABS [25]
<i>θ</i> Range for data collection [°]	3.24 to 25.99	2.00 to 30.04
Index ranges	-12 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 10 0 ≤ <i>l</i> ≤ 10	-14 ≤ <i>h</i> ≤ 14 -9 ≤ <i>k</i> ≤ 9 -18 ≤ <i>l</i> ≤ 19
Reflections collected	1320	9905
Independent reflections	681 [<i>R</i> (int) = 0.0440]	2684 [<i>R</i> (int) = 0.0364]
Refinement program	Shelxl93 [23]	Shelxl97-2 [24]
Refinement method	Full-matrix LS on <i>F</i> ²	Full-matrix LS on <i>F</i> ²
Data / restraints / parameters	681 / 0 / 38	2684 / 0 / 65
Goodness-of-fit on <i>F</i> ²	1.078	1.202
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0221 <i>wR</i> 2 = 0.0550	<i>R</i> 1 = 0.0422 <i>wR</i> 2 = 0.0891
<i>R</i> Indices [all data]	<i>R</i> 1 = 0.0252 <i>wR</i> 2 = 0.0558	<i>R</i> 1 = 0.0461 <i>wR</i> 2 = 0.0909
Extinction coefficient	0.0008(4)	0.0011(2)
Largest diff. peak and hole [e·Å ⁻³]	0.585 and -0.611	2.750 and -2.340

Table 1. Crystallographic data and refinement parameters for Li₂CsBS₃ and Cs₃BS₃.

are attacked by boron chalcogenides at temperatures above 400 °C forming silicon-chalcogen compounds by B-Si exchange at the surface of the ampoules. For the synthesis of pure samples the reaction vessel must either be made of boron nitride or graphite, or silica tubes coated with glassy carbon must be used. The latter are prepared by slowly turning a silica ampoule filled with acetone vapour through the flame of an oxygen-hydrogen operated welding torch at about 1000 °C. In some cases, especially when longer annealing is necessary, the former type of crucibles are employed. To protect them against oxidation they are encapsulated in steel or tantalum ampoules under an argon atmosphere, and these again are enclosed in evacuated silica tubes.

The following chemicals were used as starting materials: lithium sulfide (ALFA AESAR, pow-

der, 99%), mercury sulfide (FLUKA, powder, red, 99%+), elementary cesium (STREM, 99%+), amorphous boron (ALFA AESAR, amorphous, powder, 99.99%), and sulfur (MERCK, powder, DAB 6). Cs₂S was prepared by reaction of elementary cesium with mercury sulfide according to an instruction given by Klemm *et al.* [22].

For the syntheses of Li₂CsBS₃ and Cs₃BS₃, stoichiometric amounts of the alkali metal sulfide(s), elementary boron and sulfur were ground up and filled into the carbon-coated silica tubes. Thereafter they were sealed at a pressure of approximately 6 Pa.

In the case of Li₂CsBS₃ the samples were heated in horizontal one-zone furnaces to 650 °C within 4 h and kept at this temperature for 2 h. After cooling down to 400 °C within 12 h the samples were cooled down to 200 °C within 120 h followed by subsequent cooling to room temperature.

Table 2. Atom coordinates, Wyckoff positions and thermal isotropic displacement parameters with standard deviations for Li₂CsBS₃ and Cs₃BS₃.

Atom Site	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq} ^a	
<i>Li₂CsBS₃</i> :					
Cs(1)	4c	0.00561(3)	3/4	0.55947(4)	0.0346(2)
S(1)	4c	0.04087(11)	1/4	1.01155(14)	0.0191(2)
S(2)	8d	0.22820(8)	0.45113(10)	0.77414(10)	0.0294(2)
B(1)	4c	0.1670(4)	1/4	0.8427(6)	0.0183(9)
Li(1)	8d	0.3671(5)	0.4594(6)	0.5373(6)	0.0231(10)
<i>Cs₃BS₃</i> :					
Cs(1)	4e	0.39790(4)	0.95278(6)	0.29709(3)	0.03097(13)
Cs(2)	4e	0.03995(4)	0.77642(7)	0.35755(3)	0.03122(13)
Cs(3)	4e	0.26438(6)	0.15727(7)	-0.01001(4)	0.04278(15)
S(1)	4e	0.34571(16)	0.6640(2)	0.03788(12)	0.0288(3)
S(2)	4e	0.08919(17)	0.7880(3)	0.11503(12)	0.0311(3)
S(3)	4e	0.27595(16)	0.4480(2)	0.22813(12)	0.0291(3)
B(1)	4e	0.2351(6)	0.6316(9)	0.1256(5)	0.0211(11)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij}-tensor.

Cs₃BS₃ was synthesized using a horizontal one-zone furnace by heating the samples within 6 h to 720 °C, keeping this temperature for 6 h, cooling to 520 °C in 20 h followed by a temper process to 270 °C within 150 h.

In both cases colourless crystalline products containing prismatic crystals suitable for single crystal X-ray diffraction were obtained. The products (like all other thioborates containing boron in a trigonal-planar chalcogen coordination) are extremely moisture sensitive and were therefore handled under a dry argon atmosphere in glove boxes.

Single crystal analysis

For the data collection single crystals of the compounds were prepared in sealed MARK capillaries under an argon atmosphere. The X-ray diffraction data for Li₂CsBS₃ were collected on a SIEMENS P3 four-circle diffractometer, while Cs₃BS₃ was measured on a BRUKER AXS APEX system. The space groups were determined from systematic absences and intensity statistics. A reasonable structure solution for Li₂CsBS₃ was possible in space group *Pnma* (no. 62). Cs₃BS₃ crystallizes isotypic to the rubidium compound in space group *P2₁/c* (no. 14). Structure solutions were achieved by applying direct statistical methods of phase determination using the SHELXTL PLUS software [23]; full-matrix least-squares refinements were carried out using the SHELXL-97 program [24].

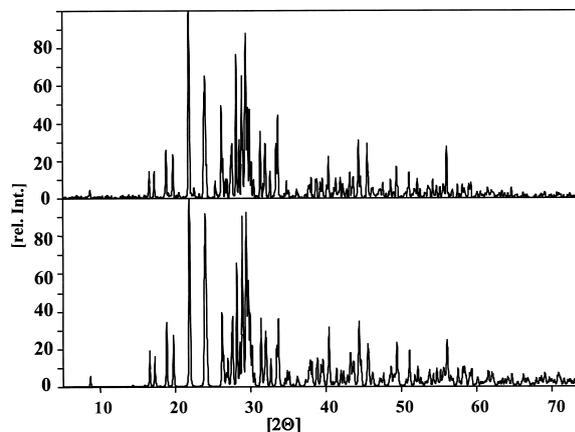


Fig. 1. X-Ray powder pattern of Cs₃BS₃. Top: experimental (Cu-K_{α1} radiation); bottom: calculated.

The parameters of the data collections as well as details of the structure solutions and refinements are summarized in Table 1. The coordinates of all atoms, equivalent isotropic displacement parameters and their estimated standard deviations are given in Table 2.

Further details of the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Zusammenarbeit, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-411530 for Li₂CsBS₃ and CSD-391170 for Cs₃BS₃, the names of the authors and this journal.

X-ray powder diffraction

For powder diffraction experiments the pulverized substance was placed between two sheets of gasproof adhesive foil and measured in transmission geometry on a STOE & CIE powder diffractometer (STADI P) with copper K_{α1}-radiation. The measured standard of the adhesive foil was subtracted from the data record. The obtained powder pattern of Cs₃BS₃ is illustrated in the upper part of Fig. 1. The lower part of Figure 1 shows a diagram created with the software pertaining to the powder diffractometer [26] which was computable on the basis of the single crystal data.

All theoretical reflection positions are observed in the measured diagram at the same position and with comparable strength. The few weak reflections not appearing in the computed one can be assigned to Cs₂S.

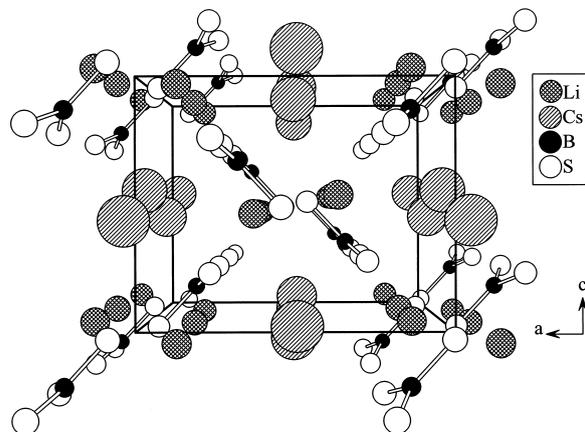


Fig. 2. Perspective view of the unit cell of Li₂CsBS₃ along [010].

Results and Discussion

Like Li₃BS₃, Na₃BS₃, K₃BS₃ and Rb₃BS₃ both crystal structures of the novel orthothioborates contain isolated planar [BS₃]³⁻ anions and coordinating alkali metal cations. A structural similarity to other known orthothioborates, for example LiSrBS₃ [7], LiBaBS₃ [8], Sr_{4,2}Ba_{2,8}(BS₃)₄S [27], K₄Ba₁₁(BS₃)₈S, KBa₄(BS₃) [28] and Tl₃BS₃ [9] is obvious since all of these compounds contain the same isolated anion entity. A more detailed description of each single thioborate is given below.

Li₂CsBS₃: The crystal structure of the lithium cesium orthothioborate consists of isolated, planar [BS₃]³⁻ anions as well as Li⁺ and Cs⁺ cations. A close structural relationship is obvious to other quaternary lithium orthothioborates such as LiSrBS₃ and to Li₃BS₃. The three B-S distances differ only insignificantly from the mean value of 1.825 Å which is comparable to that found in other thioborates with trigonal-planar coordinated boron (Li₃BS₃: 1.829 Å). The mean deviation from a best plane through the four atoms of the [BS₃]³⁻ anions is negligibly small (0.019 Å).

Fig. 2 depicts the unit cell of Li₂CsBS₃ in a perspective view along the *b*-axis. The arrangement of the anions in Li₂CsBS₃ can be described as two interpenetrating layered substructures running perpendicularly to [1 0 1] and [1 0 -1], respectively. The dihedral angle between neighbouring anions is 87.1°. For LiSrBS₃ and Li₃BS₃ this angle is 79.9° and 42.8° while in Na₃BS₃, Tl₃BS₃ and Sr₃(BS₃)₂ the anions show a parallel arrangement.

Table 3. Bond lengths and bond angles with standard deviations for Li₂CsBS₃.

B(1)-S(1)	1.858(5)	S(1)-B(1)-S(2)	117.06(13)
B(1)-S(2)	1.809(2)	S(1)-B(1)-S(2b)	117.06(13)
B(1)-S(2b)	1.809(2)	S(2)-B(1)-S(2b)	125.6(3)
Cs(1)-S(1e)	3.4981(14)	Cs(1)-S(2)	3.6995(10)
Cs(1)-S(2b)	3.6995(10)	Cs(1)-S(2m)	3.8727(10)
Cs(1)-S(2p)	3.8727(10)	Cs(1)-S(2h)	3.9021(10)
Cs(1)-S(2l)	3.9021(10)	Cs(1)-S(2d)	3.9153(11)
Cs(1)-S(2c)	3.9153(11)		
Li(1)-S(2)	2.366(5)	Li(1)-S(2p)	2.438(5)
Li(1)-S(1g)	2.446(5)	Li(1)-S(1p)	2.509(5)

a) $x, \frac{1}{2} - y, z$; b) $x, \frac{3}{2} - y, z$; c) $-x, \frac{1}{2} + y, 1 - z$; d) $-x, 1 - y, 1 - z$; e) $-x, 1 - y, 2 - z$; f) $-x, 2 - y, 1 - z$; g) $\frac{1}{2} + x, y, \frac{3}{2} - z$; h) $-\frac{1}{2} + x, y, \frac{3}{2} - z$; i) $-\frac{1}{2} + x, y, \frac{1}{2} - z$; j) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$; k) $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} - z$; l) $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{3}{2} - z$; m) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$; n) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; o) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; p) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$.

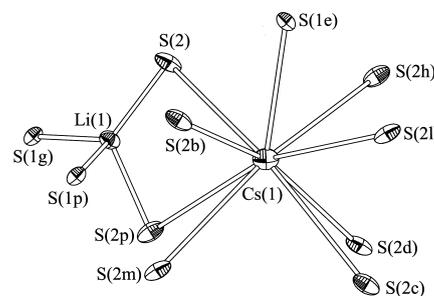


Fig. 3. Metal-sulfur coordination in Li₂CsBS₃ in an ellipsoidal presentation (50% probability).

The mean Cs-S distance of 3.809 Å is slightly longer than values found in other combinations with ninefold sulfur coordination of cesium (*cf.* Cs₂B₂S₄: 3.690 Å [10]).

The lithium atom is tetrahedrally surrounded by four sulfur atoms with a mean distance of 2.440 Å which is typical for lithium-sulfur coordination in thioborates (Li₃BS₃ 2.476 Å [6, 7], LiBaB₃S₆ 2.50 Å [8]). Fig. 3 shows the first coordination sphere of the cations in an ellipsoidal representation (50% probability). The corresponding M-S and B-S distances as well as the S-B-S angles are summarized in Table 3.

The crystallographic facts exclude a potential mobility of the lithium ions since the single lithium position in Li₂CsBS₃ is fully occupied as observed for other lithium containing orthothioborates such as Li₃BS₃, LiSrBS₃ [6, 7] and LiBaBS₃ [8]. A Li-Li distance of about 4.5 Å is too large for a Li diffusion pathway.

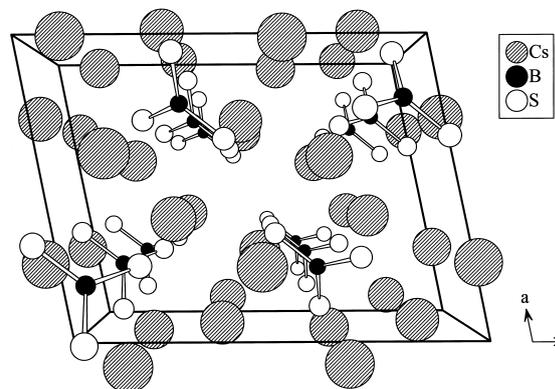
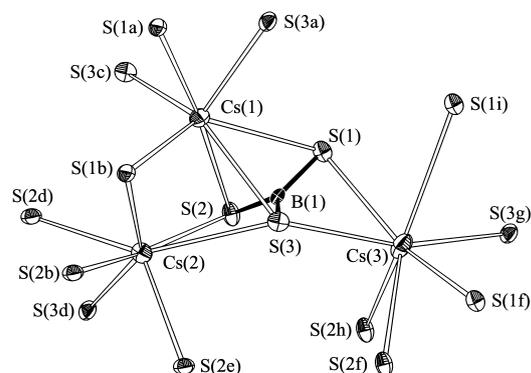
Table 4. Bond lengths and bond angles with standard deviations for and Cs₃BS₃.

B(1)-S(1)	1.826(7)	S(1)-B(1)-S(2)	120.2(4)
B(1)-S(2)	1.822(7)	S(1)-B(1)-S(3)	119.5(4)
B(1)-S(3)	1.842(7)	S(2)-B(1)-S(3)	120.3(4)
Cs(1)-S(1a)	3.433(2)	Cs(1)-S(3a)	3.475(2)
Cs(1)-S(1b)	3.514(2)	Cs(1)-S(3c)	3.592(2)
Cs(1)-S(3)	3.650(2)	Cs(1)-S(2)	3.812(2)
Cs(1)-S(1)	3.963(2)		
Cs(2)-S(2)	3.441(2)	Cs(2)-S(3d)	3.457(2)
Cs(2)-S(2b)	3.469(2)	Cs(2)-S(2e)	3.567(2)
Cs(2)-S(1b)	3.638(2)	Cs(2)-S(2d)	3.708(2)
Cs(2)-S(3)	3.951(2)		
Cs(3)-S(1f)	3.423(2)	Cs(3)-S(1)	3.509(2)
Cs(3)-S(3g)	3.659(2)	Cs(3)-S(2f)	3.672(2)
Cs(3)-S(2h)	3.692(2)	Cs(3)-S(3)	3.759(2)
Cs(3)-S(1i)	4.313(2)		

a) $1-x, 1/2+y, 1/2-z$; b) $x, 3/2-y, 1/2+z$; c) $x, 1+y, z$; d) $-x, 1/2+y, 1/2-z$; e) $-x, -1/2+y, 1/2-z$; f) $x, -1+y, z$; g) $x, 1/2-y, -1/2+z$; h) $-x, 1-y, -z$; i) $x, 3/2-y, -1/2+z$; j) $x, 1/2-y, 1/2+z$; k) $1-x, -1/2+y, 1/2-z$; l) $1-x, 1-y, -z$.

Cs₃BS₃: As mentioned before, the new compound crystallizes isotypic to Rb₃BS₃ in space group *P2₁/c* (no. 14). The structure can be described as stacks of [BS₃]³⁻ anions arranged along the crystallographic *b*-axis as illustrated by Fig. 4 in a perspective view of the unit cell. The B-S distances vary from 1.822 to 1.842 Å (mean 1.830 Å), the S-B-S angles differ at most 0.4° from the ideal trigonal planar coordination angle. The cesium cations are surrounded by seven sulfur atoms forming an irregular polyhedron. Cs(3) is coordinated within a 4 Å radius by six sulfur atoms but completes the seven-fold coordination with an additional sulfur atom in a distance of 4.313 Å (see Fig. 5). B-S bond lengths, S-B-S bond angles and Cs-S distances are summarized in Table 4.

With the preparation of crystalline Cs₃BS₃ we were able to complete the series of ternary alkaline thioborates. The synthesis of Li₂CsBS₃ shows that

Fig. 4. Perspective view of the unit cell of Cs₃BS₃ along [010].Fig. 5. Metal-sulfur coordination in Cs₃BS₃ in an ellipsoidal presentation (50% probability).

mixed alkali metal thioborates of a defined composition can be stabilized. A tendency concerning the arrangement of the BS₃ units is still unpredictable.

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